

## **APPENDIX C**

### **Laboratory Results Report**



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Secretary for  
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# Air Resources Board

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Special Analysis Section  
Northern Laboratory Branch

DATE: February 7, 2007

SUBJECT: 2006 CARBON DISULFIDE ANALYSIS AFTER APPLICATION OF  
SODIUM TETRATHIOCARBONATE IN KERN COUNTY

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The Special Analysis Section (SAS) provided laboratory support for the sodium tetrathiocarbonate application air monitoring program conducted in Kern County, November 2006. The SAS laboratory received 71 samples collected over a five-day period. The samples were collected in six-liter Silco<sup>TM</sup> canisters. The SAS laboratory analyzed for carbon disulfide, the pesticidal agent and break down product of sodium tetrathiocarbonate.

The data are presented in the attached report, titled "Carbon Disulfide Method Development and Analytical Results for Kern County Air Monitoring Samples Collected in Six-liter Silco<sup>TM</sup> Canisters after Application of Sodium Tetrathiocarbonate." If you have any questions or comments, please contact Ms. Karen Fletcher of my staff at 322-2430 or me at 322-2496.

Attachment

cc: Michael Poore  
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*The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our website: <http://www.arb.ca.gov>.*

California Environmental Protection Agency

# California Environmental Protection Agency

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## **Air Resources Board**

### **Carbon Disulfide Method Development and Analytical Results for Kern County Air Monitoring Samples Collected in Six-liter Silco™ Canisters after Application of Sodium Tetrathiocarbonate**

**Date: December 2006**

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This report has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

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## 1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct air monitoring for carbon disulfide after the drip irrigation application of sodium tetrathiocarbonate using six-liter Silco™ canisters for sample collection. ARB staff analyzed air samples collected during a five day period at eight Kern County monitoring sites. This report covers the analytical and quality assurance results for this application air-monitoring program. The standard operating procedure (SOP) for the analysis of carbon disulfide is attached as Appendix 1. DPR requested an estimated quantitation limit (EQL) for carbon disulfide of 0.5 µg/m<sup>3</sup>.

## 2.0 METHOD DEVELOPMENT AND STANDARD OPERATING PROCEDURE

### 2.1 Overview

The method follows U. S. Environmental Protection Agency (USEPA) Compendium Method TO-15. Each field sample is pressurized to approximately 5 pounds per square inch gauge (psig) before sample analysis. The canister samples are concentrated using a cryogenic autosampler/concentrator (cryosampler) and then loaded onto the capillary column. The cryosampler contains a Nafion dryer, which reduces water vapor in the sample stream. A gas chromatograph equipped with a high-resolution capillary column separates the sample components. A quadrapole mass spectrometer operated in selected ion monitoring (SIM) mode detects the sample components. The results of the analysis are calculated using an internal standard method.

### 2.2 Instrument Reproducibility

In order to establish the reproducibility of this method, staff analyzed a spiked standard of carbon disulfide at three different levels. Staff analyzed each standard level five times. Table 1 shows the instrument reproducibility results for carbon disulfide.

### 2.3 Calibration

The gas chromatograph is calibrated using an internal standard method. A calibration curve is constructed by linear regression analysis of calibrator results. The high point of the calibration is determined by sampling 200 ml of a canister containing the high point concentration. Subsequent calibration points are determined by injecting smaller amounts from the standard canister. The subsequent calibration points' volumes are 100, 50, 25 and 15 ml. Calibration curves used for the current study had an  $r^2$  value (variance) equal to or greater than 0.993. The instrument is calibrated before each new batch of samples, and if any of the following occur: calibration check is not within 20% of its target value, the Laboratory Control Sample (LCS) is not within control limits, the instrument needs retuning, or the instrument requires maintenance.

## 2.4 Minimum Detection Limit (MDL)

This method follows standard USEPA procedures to calculate the MDL. Using the analysis of seven low-level matrix spikes the MDL, Limit of Detection (LOD) and EQL for a 200-ml sample are calculated as follows:

s = the standard deviation of the concentration calculated for the seven replicate spikes.

For Carbon Disulfide:  $s = 0.02136 \mu\text{g}/\text{m}^3$   
 $\text{MDL} = (3.14) * (s) = (3.14) * (0.021) = 0.067 \mu\text{g}/\text{m}^3$   
 $\text{EQL} = (5) * (\text{MDL}) = (5) * (0.067) = 0.335 \mu\text{g}/\text{m}^3$   
Assume 1:1.79 dilution for pressurization of sample;  
 $\text{LOD} = 0.067 \text{ ng}/\text{m}^3 * 1.79 = 0.120 \mu\text{g}/\text{m}^3$   
 $\text{EQL} = 0.335 \text{ ng}/\text{m}^3 * 1.79 = 0.600 \mu\text{g}/\text{m}^3$

The dilution factor reflects the estimated dilution of the field sample when the canister is pressurized to approximately five (5) psig just prior to analysis. This dilution factor is used to adjust the EQL value and must be factored in for actual quantification of samples.

For results above the EQL the lab reports these values to two (2) significant figures. Results below the EQL but greater than or equal to the LOD are reported to one (1) significant figure. If a result is less than LOD it is reported as less than the calculated LOD for that sample. The less than LOD value is reported to one (1) significant figure.

The requested EQL for carbon disulfide is  $0.50 \mu\text{g}/\text{m}^3$ . Based on a 200-ml sample size the EQL achieved was  $0.600 \mu\text{g}/\text{m}^3$ . The maximum sample size was set at 200 ml based on the increased probability of matrix interference from high levels of sample moisture and matrix.

## 2.5 Collection Efficiency (Recovery)

Carbon disulfide is listed in USEPA Compendium Method TO-15. Staff did not evaluate carbon disulfide for collection efficiency.

## 2.6 Storage Stability

Carbon disulfide is listed in USEPA Compendium Method TO-15. Compounds listed for this method are considered stable in the collection canister for 30 days. The trip, field, and lab spikes were prepared in excess of 30 days prior to analysis and all spikes demonstrated excellent recovery. All field samples were analyzed within 24 days of sample collection.

## 2.7 *Canister Cleaning*

Canisters are cleaned in batches of eight (8). Staff chooses one of the cleaned canisters for GCMS analysis. Normally, staff analyzes the canister with the highest level of target compound. If results for the target compounds are not below method LOD the entire cleaning batch is re-cleaned and rechecked. Appendix 2 contains the standard operating procedure for canister cleaning.

## 3.0 **APPLICATION AIR MONITORING SAMPLE RESULTS**

The laboratory received 71 air samples from Kern County, including four (4) each of trip blanks, trip spikes, and field spikes. Four (4) lab spikes were prepared and held in the laboratory. Table 2 contains the results for the analysis of the carbon disulfide air samples following the application of sodium tetrathiocarbonate.

All field samples were initially analyzed using 200 ml of sample. Those samples that had results greater than the highest calibration level were reanalyzed. In most cases the samples were reanalyzed using a smaller sample volume. Three field samples were diluted by pressurizing the sample canister to approximately 30 psig and then reanalyzed at a smaller sample volume. Results were multiplied by the pressurizing dilution and the sample volume ratio (200 ml/volume injected) to calculate the actual concentration.

## 4.0 **ANALYTICAL QUALITY CONTROL**

### 4.1 *Laboratory System Blanks*

The laboratory system blank checks the analytical system for contamination. A laboratory system blank, which is 200 ml of ultra pure nitrogen, is run before the start of an analytical batch, and before and after a continuing calibration standard. Staff defines an analytical batch as the samples in an automated GC/MS analytical sequence.

Three system blank results were above the LOD, but less than the EQL. These blanks followed samples of very high concentration; all subsequent blanks during the run were below the limit of detection. No further action was taken.

All other system blank results were less than the limit of detection (<LOD).

### 4.2 *Method Calibration*

The analytical method uses a certified gas standard for calibration. Before analysis, the detector is autotuned and the results are evaluated using the criteria listed in Appendix 3. The certified standard used for the current project was obtained from Scott-Marrin, Inc. and has the following specifications: carbon disulfide 0.457 ppm/v, analytical accuracy +/- 5%, Cylinder #FA02705. Staff prepares working calibration gas by diluting the certified stock standard to produce the calibration curve detailed in Appendix 4.



### *4.3 Laboratory Duplicate Samples*

Staff analyzed approximately 10% of the ambient air samples as duplicates. Results of these duplicate analyses appear in Table 3.

### *4.4 Laboratory Control Samples*

Analysis of a laboratory control sample (LCS) occurs with each analytical batch. The stock standard for LCS preparation should not be the same stock standard used to calibrate the instrument. The certified standard used for the current project was obtained from Scott-Marrin, Inc. and has the following specifications: carbon disulfide 0.406 ppm/v, analytical accuracy +/- 5%, Cylinder #FA02632. The LCS is prepared by spiking the stock standard into a six-liter canister and diluting to a specific concentration with ultrapure nitrogen. A 200-ml LCS sample is analyzed with each analytical batch.

Acceptance range for carbon disulfide used during the current program is 96.07 to 106.73 %. All LCS results were within the acceptance criteria. Results of the LCS analyses are tabulated in Table 4.

### *4.5 Continuing Calibration Verification Standard*

Staff includes a continuing calibration verification standard (CCV) at the beginning of each analytical batch, after every tenth sample in an analytical sequence and at the end of each analytical batch. The CCV must be within  $\pm 20\%$  of the expected value. If the CCV is outside of limits, staff takes appropriate corrective action, and then reanalyzes the CCV and the affected samples. Calibration of the entire system occurs if the reanalysis of the CCV is outside of acceptance limits. A summary of the average percent recovery for the CCV is reported in Table 5.

## **5.0 LABORATORY, TRIP, FIELD SPIKES AND TRIP BLANKS**

Four (4) each of laboratory spikes, trip spikes, field spikes and trip blanks were analyzed during the 2006 Kern County application air study. The staff held the lab spikes in the laboratory and analyzed them with the field samples. The stock standard used for spikes was the same standard used to prepare the laboratory control standard.

### *5.1 Laboratory spikes*

Four (4) canisters were spiked and stored at ambient temperature in the laboratory. The lab spikes are pressurized to approximately five (5) psig with ultra pure nitrogen and analyzed. Table 6 presents the laboratory spike results.

### *5.2 Trip spikes*

Four (4) canisters were spiked and taken into the field along with the field sample canisters. The trip spike accompanies field staff to the field and is returned to the

laboratory. Trip spikes do not undergo field sampling. Table 7 presents the trip spike results.

### *5.3 Field spikes*

Four (4) canisters were spiked and taken into the field along with the field sample canisters. Sampling of the field spikes occurred at a co-located monitoring site. Introduction of ambient air into the spiked canisters follows the ambient air sampling protocol. Field spike results were not corrected for background levels. The field spike results are reported in Table 8.

### *5.4 Trip blanks*

The lab received four (4) trip blank canisters. A trip blank is an evacuated six-liter canister. Trip blank canisters accompany field staff through the sampling process. The trip blanks are pressurized to approximately five (5) psig with ultra pure nitrogen and analyzed. Table 9 presents the trip blank results. All results were less than the LOD.

## **6.0 DISCUSSION**

The laboratory received 59 field samples and 12 field quality control samples. Four (4) each of trip blanks, field spikes and trip spikes were received by the laboratory. Four (4) additional laboratory spikes were prepared and held at the laboratory. Results for carbon disulfide ranged from  $0.33 \mu\text{g}/\text{m}^3$  to  $198 \mu\text{g}/\text{m}^3$ . All field sample results were above the LOD of  $0.12 \mu\text{g}/\text{m}^3$ . The results of six samples fell between the LOD and EQL. Thirty-seven samples had results greater than the EQL.

Three samples (NS-CD2, NWC-CD2, and WS-CD2) required a dilution greater than 13.3 fold. The dilutions were achieved by repressurizing the sample canister to approximately thirty (30) psig and then analyzing a smaller sample volume. The final dilution factors of NS-CD2, NWC-CD2, and WS-CD2 were 62.54, 39.67, and 58.89 respectively.

The three system blanks that followed samples NS-CD2, NWC-CD2, and SEC-CD2 had values between the LOD and EQL. This was most likely carry over from the highly concentrated samples. All prior and subsequent system blanks were <LOD; no further action was taken.

Of the 59 field samples received, fourteen (14) were invalidated due to all final sampling pressures reading less than -10 inches of mercury after sample collection. Two additional samples were invalidated due to sampler malfunction. These samples were not analyzed. No other anomalous results were observed for the field samples.

No other anomalous events occurred during this study.

**Table 1: Instrument Reproducibility Carbon Disulfide**

<b>Target Concentration</b>	<b>Low Level (ng/m<sup>3</sup>)</b>	<b>Mid Level (ng/m<sup>3</sup>)</b>	<b>High Level (ng/m<sup>3</sup>)</b>
<b>Sample Number</b>			
1	392.43	1721.25	3485.28
2	381.60	1712.55	3501.93
3	381.94	1709.91	3440.12
4	382.07	1711.28	3423.73
5	383.91	1700.71	3458.64
<b>Average</b>	<b>384.39</b>	<b>1711.14</b>	<b>3461.94</b>
<b>SD</b>	<b>4.58</b>	<b>7.32</b>	<b>31.98</b>
<b>RSD</b>	<b>1.19</b>	<b>0.43</b>	<b>0.92</b>

**TABLE 2: Kern County Application Monitoring Results**

Site	Log Number	Sample Identification	Canister Number	Date Received	Date Analyzed	Results (µg/m3)	
						Carbon Disulfide	Dilution
ES	15	ES-CD1	1177	11/20/2006		INVALID	
	32	ES-CD2	1089	11/20/2006	12/6/2006	4.0E+01	28.06
	41	ES-CD3	1175	11/20/2006	12/7/2006	6.9E+00	2.00
	50	ES-CD4	1107	11/20/2006	12/7/2006	9.6E-01	1.89
	59	ES-CD5	1170	11/20/2006		INVALID	
	68	ES-CD6	1186	11/20/2006		INVALID	
	71	ES-CD6-a	1182	11/20/2006	12/11/2006	<b>6E-01</b>	2.00
NEC	7	NEC-CD-B	1173	11/20/2006	11/28/2006	<b>3E-01</b>	2.06
	16	NEC-CD1	1060	11/20/2006		INVALID	
	33	NEC-CD2	1139	11/20/2006		INVALID	
	42	NEC-CD3	1152	11/20/2006		INVALID	
	51	NEC-CD4	1167	11/20/2006		INVALID	
	60	NEC-CD5	1063	11/20/2006	12/8/2006	9.5E-01	1.90
	69	NEC-CD6	1178	11/20/2006	12/11/2006	7.2E-01	1.98
NS	17	NS-CD1	1062	11/20/2006		INVALID	
	34	NS-CD2	1122	11/20/2006	12/6/2006	1.2E+02	62.54
	43	NS-CD3	1162	11/20/2006	12/8/2006	1.5E+01	7.97
	52	NS-CD4	1061	11/20/2006	12/8/2006	1.3E+01	7.79
	61	NS-CD5	1125	11/20/2006	12/8/2006	5.0E+00	1.89
	70	NS-CD6	1132	11/20/2006	12/11/2006	2.8E+00	1.98
NWC	1	NWC-CD-B	1165	11/20/2006		INVALID	
	9	NWC-CD1	1069	11/20/2006		INVALID	
	26	NWC-CD2	1064	11/20/2006	12/1/2006	1.4E+02	39.67
	35	NWC-CD3	1136	11/20/2006	12/6/2006	1.1E+01	7.67
	44	NWC-CD4	1097	11/20/2006		INVALID	
	53	NWC-CD5	1092	11/20/2006	12/8/2006	5.1E+00	1.96
	62	NWC-CD6	1083	11/20/2006	12/12/2006	1.2E+01	3.97
SEC	5	SEC-CD-B	1057	11/20/2006	11/28/2006	<b>3E-01</b>	2.04
	13	SEC-CD1	1161	11/20/2006		INVALID	
	14	SEC-CD1-C	1158	11/20/2006		INVALID	
	30	SEC-CD2	1098	11/20/2006	12/1/2006	5.1E+01	15.80
	31	SEC-CD2-C	1179	11/20/2006	12/6/2006	5.3E+01	28.06
	39	SEC-CD3	1134	11/20/2006	12/5/2006	3.6E+00	1.95
	40	SEC-CD3-C	1099	11/20/2006	12/7/2006	3.7E+00	2.04
	48	SEC-CD4	1196	11/20/2006	12/7/2006	<b>4E-01</b>	1.88
	49	SEC-CD4-C	1073	11/20/2006	12/7/2006	<b>4E-01</b>	1.99
	57	SEC-CD5	1053	11/20/2006	12/8/2006	1.5E+00	1.91
	58	SEC-CD5-C	1071	11/20/2006	12/8/2006	1.4E+00	1.95
	66	SEC-CD6	1137	11/20/2006	12/11/2006	5.7E-01	1.87
	67	SEC-CD6-C	1138	11/20/2006	12/11/2006	<b>6E-01</b>	1.92

**TABLE 2: Kern County Application Monitoring Results**

Site	Log Number	Sample Identification	Canister Number	Date Received	Date Analyzed	Results (µg/m3)	
						Carbon Disulfide	Dilution
SS	12	SS-CD1	1065	11/20/2006		INVALID	
	29	SS-CD2	1058	11/20/2006	12/1/2006	6.1E+01	15.88
	38	SS-CD3	1070	11/20/2006	12/5/2006	5.0E+00	1.94
	47	SS-CD4	1160	11/20/2006	12/7/2006	8.8E-01	2.04
	56	SS-CD5	1144	11/20/2006	12/8/2006	1.0E+00	2.00
	65	SS-CD6	1180	11/20/2006	12/11/2006	6.8E-01	2.00
SWC	3	SWC-CD-B	1171	11/20/2006		INVALID	
	11	SWC-CD1	1141	11/20/2006	11/29/2006	3.0E+01	16.84
	28	SWC-CD2	1082	11/20/2006	12/1/2006	5.7E+01	15.28
	37	SWC-CD3	1142	11/20/2006	12/6/2006	9.6E+00	3.85
	46	SWC-CD4	1112	11/20/2006	12/7/2006	3.2E+00	1.92
	55	SWC-CD5	1056	11/20/2006	12/8/2006	8.1E-01	1.98
	64	SWC-CD6	1093	11/20/2006	12/11/2006	7.8E-01	1.80
WS	10	WS-CD1	1074	11/20/2006		INVALID	
	27	WS-CD2	1066	11/20/2006	12/1/2006	2.0E+02	58.89
	36	WS-CD3	1091	11/20/2006	12/6/2006	2.3E+01	16.19
	45	WS-CD4	1176	11/20/2006	12/8/2006	2.1E+01	7.79
	54	WS-CD5	1101	11/20/2006	12/8/2006	2.9E+00	1.97
	63	WS-CD6	1105	11/20/2006	12/11/2006	5.3E+00	1.95

**Notes:**

No analytical results were less than the calculated LOD.

If an analytical result is  $\geq$  LOD and  $<$  EQL it is reported in the table to one significant figure and is **Bold**. Levels  $\geq$  EQL are reported as the actual measured value and are reported to two significant figures.

INVALID: Data not collected for this sample. Sample pressure less than -10 inches Mercury upon receipt by lab or sampler malfunction.

Site identification codes –B after the site identifiers are background samples.

Site identification codes -C after the site identifiers are collocated samples for the samples with the corresponding run number.

Field QC sample log numbers reported in a separate table.

Field Site location identification:

ES: East Side

NEC: Northeast Corner

NS: North Side

NWC: Northwest Corner

SEC: Southeast Corner

SS: Southside

SWC: Southwest Corner

WS: Westside

**TABLE 3: Laboratory Duplicate Precision for Carbon Disulfide**

Log Number	Sample Identification	Date Received	Date Analyzed	Carbon Disulfide (µg/m3)	
				Results	Relative %Difference
26	NWC-CD2	11/20/2006	12/1/2006	140.68 140.91	0.16
35	NWC-CD3	11/20/2006	12/6/2006	108.90 108.60	-0.28
48	SEC-CD4	11/20/2006	12/7/2006	0.37 0.36	-2.74
52	NS-CD4	11/20/2006	12/8/2006	13.22 13.19	-0.23
61	NS-CD5	11/20/2006	12/8/2006	4.99 5.03	0.80
71	ES-CD6-a	11/20/2006	12/11/2006	0.64 0.66	3.08

Note:

Relative % Difference:  $\text{Result B} - \text{Result A} / (\text{Average of Result A and B}) * 100$

**TABLE 4: Laboratory Control Sample Results**

Date	Time	Carbon Disulfide		
		Expected ( $\mu\text{g}/\text{m}^3$ )	Actual ( $\mu\text{g}/\text{m}^3$ )	Recovery (%)
28-Nov-06	16:08	3.49	3.52	101.04
29-Nov-06	10:34	3.49	3.52	100.81
30-Nov-06	19:50	3.49	3.47	99.35
1-Dec-06	11:06	3.49	3.53	101.27
5-Dec-06	13:23	3.49	3.48	99.92
6-Dec-06	10:06	3.49	3.50	100.39
7-Dec-06	18:29	3.49	3.49	99.99
8-Dec-06	10:22	3.49	3.58	102.73
11-Dec-06	15:10	3.49	3.65	104.64
12-Dec-06	9:37	3.49	3.62	103.90

**TABLE 5: Continuing Calibration Verification Standard Results Summary**

Analyte	Average Expected Concentration ( $\mu\text{g}/\text{m}^3$ )	Average Actual Concentration ( $\mu\text{g}/\text{m}^3$ )	Average Percent Recovery	Average Percent Standard Deviation
Carbon Disulfide	3.93	3.96	100.71	0.81

**TABLE 6: Laboratory Spike Results**

Date	Sample ID	Canister Number	Carbon Disulfide		
			Expected ( $\mu\text{g}/\text{m}^3$ )	Actual ( $\mu\text{g}/\text{m}^3$ )	Recovery (%)
11/28/2006	06CS2LS01	1102	4.69	5.06	107.87
11/30/2006	06CS2LS02	1111	4.60	4.97	108.06
12/5/2006	06CS2LS03	1051	4.72	5.14	108.99
12/6/2006	06CS2LS04	1067	4.65	5.07	109.19

**TABLE 7: Trip Spike Results**

Date	Sample ID	Canister Number	Carbon Disulfide		
			Expected ( $\mu\text{g}/\text{m}^3$ )	Actual ( $\mu\text{g}/\text{m}^3$ )	Recovery (%)
11/28/2006	06CS2018	1126	4.51	5.10	113.17
11/30/2006	06CS2019	1172	4.55	4.80	105.33
12/5/2006	06CS2020	1128	4.74	5.19	109.53
12/8/2006	06CS2021	1087	4.67	5.13	109.83

**TABLE 8: Field Spike Results**

Date	Sample ID	Canister Number	Carbon Disulfide		
			Expected ( $\mu\text{g}/\text{m}^3$ )	Actual ( $\mu\text{g}/\text{m}^3$ )	Recovery (%)
11/28/2006	06CS2002	1129	4.62	5.17	111.85
11/30/2006	06CS2004	1086	4.55	4.89	107.34
12/5/2006	06CS2006	1135	4.67	5.15	110.32
12/6/2006	06CS2008	1140	4.58	4.88	106.68

Note: Results not corrected for background levels.



**TABLE 9: Trip Blank Results**

Sample Identification	Canister Number	Date Received	Date Analyzed	Carbon Disulfide		Dilution
				$\mu\text{g}/\text{m}^3$	LOD ( $\mu\text{g}/\text{m}^3$ )	
CD-TB1	1066	11/20/2006	11/28/2006	<LOD	0.12	1.82
CD-TB2	1153	11/20/2006	11/30/2006	<LOD	0.12	1.83
CD-TB3	1052	11/20/2006	12/5/2006	<LOD	0.12	1.78
CD-TB4	1085	11/20/2006	12/6/2006	<LOD	0.12	1.78

## **Appendices: 1 through 4**

## **Appendix 1**

### *Standard Operating Procedure for the Sampling and Analysis of Carbon Disulfide in Silco™ Canisters*

# California Environmental Protection Agency

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# Air Resources Board

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

**Standard Operating Procedure  
Sampling and Analysis of Carbon Disulfide  
In Silco™ Canisters Using a Varian  
Stand Alone Cryogenic Sampler**

**August 2006  
Revision 3**

Approved by:

Russell Grace, Manager  
Special Analysis Section

This SOP has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

## SCOPE

This method, which follows closely EPA Method TO-15, is for the sampling and analysis of carbon disulfide (CS<sub>2</sub>) using six-liter Silco™ canisters for sample collection. Collected samples are analyzed by gas chromatography/mass spectrometry using a cryogenic sampler.

## 2. SUMMARY OF METHOD

Ambient air is collected into evacuated six-liter Silco™ canisters using a sub-atmospheric pressure collection mode. Sample canisters are subsequently pressurized in the laboratory to approximately five (5) pounds per square inch gauge (psig) and analyzed by Gas Chromatography / Mass Spectrometry (GC/MS) using a cryogenic concentrator to prepare the air sample. Samples are analyzed in the Selected Ion Monitoring (SIM) mode using bromomethane-d<sub>3</sub> as the primary internal standard for quantitation, and 1,2-dichloropropane-d<sub>6</sub> as a secondary internal standard. 1,2-dichloropropane-d<sub>6</sub> is used to evaluate bromomethane-d<sub>3</sub> for interference. Estimated quantitation level for this method is 0.6 µg/m<sup>3</sup>.

## 3. INTERFERENCES/LIMITATIONS

Interference may result from improperly cleaned canisters. Analysis of samples containing high concentrations of early eluting pesticide components may cause significant contamination of the analytical equipment. Co-eluting compounds trapped during sample collection may interfere. Running canister blanks and system blanks should minimize contamination originating in the analytical instrument.

## 4. EQUIPMENT AND CONDITIONS

### A. Instrumentation

Hewlett Packard 5890 Series II gas chromatograph:

Detector: 280° C

Injector: 220° C

Column: Restek Rtx-200, 60 meter, 0.32mm I.D., 1.5 micron film thickness

GC temperature program: initial -10° C, -10 to 80° C @ 10° C/min, 80° to 200° C @ 25° C/min, hold for 1 minute, 200 to 240° C @ 25° C/min

Carrier Gas: Helium, grade 5 or better

Hewlett Packard 5973 mass selective detector:

Acquisition Mode: SIM

Tune File: PFTBA Autotune, maximum sensitivity

Ions monitored: 76 m/z quant, 78 m/z qualifier

Varian Stand Alone cryogenic concentrator:

Valve Oven: 60° C  
Autosampler Oven: 60° C  
Nafion Dryer: ambient  
Sample Line: 150° C  
Cryotrap: -180° C to 150° C  
Transfer Line: 150° C  
Cryofocus: -180° C to 150° C  
Sample Size: 100 ml  
Internal Standard Loop: 1 ml

#### B. Auxiliary Apparatus

Compressed helium: Grade 5 or better  
Compressed nitrogen: Grade 5 or better  
Liquid nitrogen for cryogenic concentrator  
Certified standard for carbon disulfide  
Restek, 6.0 liter Silcosteel™ canisters with Silcosteel™ valve  
Pressure gauge, -30 inches Mercury (Hg) to 30 pounds psig.  
Canister cleaning system

### 5. ANALYSIS OF SAMPLES

- 1) Perform a PFTBA autotune and evaluate tune criteria. Place a copy of the autotune results in the autotune folder.
- 2) Check and record the pressure in the field sample canisters. Pressurize the field sample canisters to approximately 5.0 psig with filtered Grade 5 or better nitrogen. Record the final pressure.
- 3) Prepare a sample sequence for the GC/MS. The sequence should include a continuing calibration check (CCV), and a blank, for every 10 field samples. A laboratory control sample (LCS) and a duplicate are run once per analytical batch not to exceed 20 samples. Load the sequence into the GC/MS in the remote start mode.
- 4) Prepare a sample sequence for the Varian. The sample sequence should be organized as follows: system blank, CCV, LCS, field samples, duplicate field sample, and CCV. If the CCV is not within  $\pm 20\%$  of its assigned value the system must be recalibrated.
- 5) Attach the sample canisters to the Varian autosampler ring as per the sequence. Execute the Varian sequence, which in turn will initiate the GC sequence.
- 6) Sample quantitation reports will print out after each analysis.
- 7) Review and edit the quantitation reports as needed.
- 8) Calculations will require a correction for the required pressurization performed prior to analysis. Instrument reports will be in units of  $\mu\text{g}/\text{m}^3$  and must be corrected for the analytical dilution using the following calculation:

$$(F_p / I_p) \times C_i = C_r$$

$I_p$  = initial canister pressure in mm Hg  
 $F_p$  = final canister pressure in mm Hg  
 $C_i$  = concentration from the analysis report in  $\mu\text{g}/\text{m}^3$   
 $C_r$  = reported concentration in  $\mu\text{g}/\text{m}^3$

## 6. QUALITY ASSURANCE

### A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows. Inject five replicate samples of  $\text{CS}_2$  standards at three concentrations, a low level close to the EQL, a mid level and a high level at the top of the calibration range.

### B. Linearity

A five-point calibration is performed. Calibration standards ranging from approximately 0.30 to 3.95  $\mu\text{g}/\text{m}^3$  are used to calibrate the method. If ambient samples are diluted times eight (8), the calibrated ambient sample range is approximately 2.40 to 31.60  $\mu\text{g}/\text{m}^3$ . The results are used to calculate calibration curves using linear or quadratic regression.

### C. Minimum Detection Limit

Detection limits are based on the US EPA MDL calculation. Using the analysis of seven replicates of a low-level matrix spike, the method detection limits (MDL) and the EQL for the pesticide components are calculated as follows:

$$\text{MDL} = 3.14*s$$

$$\text{EQL} = 5*\text{MDL}$$

Where s equals the standard deviation of the response calculated for the seven replicate spikes. The calculated MDL for  $\text{CS}_2$  is 0.067  $\mu\text{g}/\text{m}^3$ . The respective EQL is 0.335  $\mu\text{g}/\text{m}^3$ . Assuming a 1 to 1.79 dilution to pressurize the ambient samples the EQL is 0.600  $\mu\text{g}/\text{m}^3$  for  $\text{CS}_2$ .

For results above the EQL the lab reports these values to two (2) significant figures. Results below the EQL but greater than or equal to the LOD are reported to one (1) significant figure. If a result is less than LOD it is reported as less than the calculated LOD for that sample. The less than LOD value is reported to one (1) significant figure.

#### D. Storage Stability

A CS<sub>2</sub> storage stability study will not be performed. Carbon Disulfide is included in EPA Method T0-15 and as stated in section 1.3 “under conditions of normal usage for sampling ambient air, most VOC’s can be recovered from canisters near their original concentrations after storage of up to 30 days.” During this program all samples will be analyzed within 28 days of collection.

#### E. Safety Precautions

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure. All applicable safety precautions must be observed for the use of compressed gas cylinders.



## **Appendix 2**

### *Standard Operating Procedure For Cleaning Silco™ Canisters*

Northern Laboratory Branch  
Monitoring and Laboratory Division  
CALIFORNIA AIR RESOURCES BOARD

SOP MLD SAS P1, Version 1.0  
PESTICIDE SUPPORT PROGRAM

STANDARD OPERATING PROCEDURE FOR CLEANING SILCO™ CANISTERS

APPROVED BY:  
Michael P. Spears, Manager  
Special Analysis Section

November 15, 2000

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board (ARB). Specific brand names and instrument descriptions listed in the Standard Operating Procedure are for equipment used by the ARB laboratory.

## 1 INTRODUCTION

This document describes a method for cleaning six (6)-liter Silco™ canisters used for ambient air sampling of pesticides. The procedure is used to evacuate and pressurize individual canisters or groups of canisters in a heated oven.

## 2 SUMMARY OF METHOD

This method is based on EPA Method TO-14A. Up to eight (8) 6-liter canisters are connected to a manifold in an oven and evacuated to less than –30 inches of mercury. The canisters are heated to 70 degrees centigrade and purged four times with humidified ultrapure nitrogen. The purge cycling is from –30 inches mercury (Hg) to 25 pounds per square inch gauge (psig). Each cycle is 24 minutes (12 minutes vacuum and 12 minutes pressure). Both manual and automated procedures are provided. A liquid nitrogen cold trap on the vacuum line prohibits back-diffusion of the vacuum pump oil vapor and prevents water vapor from entering the vacuum pump.

## 3 INTERFERENCES AND LIMITATIONS

- 3.1 Canisters used for standards or controls may need reconditioning on a regular basis.
- 3.2 Canisters containing high pesticide concentrations may require more than one cleaning session to meet specified contamination criteria.

## 4 APPARATUS

- 4.1 Stainless steel tubing, 3/4 inch
- 4.2 Duo-Seal, two stage, vacuum pump, Edwards.
- 4.3 Stabil-Therm Electric Oven, Pro-Tronix-11.
- 4.4 Dewar, cylindrical, 1600 ml capacity, 80 mm ID, Kontes KM-611410-2116.
- 4.5 Valves, 1/2" Varian, Model # L8732-301
- 4.6 Safety glasses and cryogenic gloves
- 4.7 Valco Instruments Company Inc., Digital Valve Sequence Programmer
- 4.8 Humidifier Canister, a 6L SilcoCan™ canister filled with ≥500 ml of organic free distilled water (HPLC grade).

## 5 MATERIALS

5.1 Grade five ultra pure compressed nitrogen.

5.2 Liquid nitrogen.

5.3 HPLC grade water.

## 6 SAFETY

6.1 Do not pressurize the canisters to more than 30 psig.

6.2 Keep the liquid nitrogen dewar filled whenever the vacuum pump is running.

6.3 Do not allow trapped vacuum vapors to move into the clean part of the system.

6.4 Check vacuum pump oil level periodically. Change oil every six months.

6.5 The humidifying system (system bubbler) should always contain at least 500 ml of water for proper canister humidifying.

6.6 The nitrogen cylinder should be changed whenever the cylinder pressure drops below 500 psig.

## 7.0 PROCEDURE

7.1. Vent all canisters in the hood.

7.2. Record canister number, sample number, date, and the canister designated as the batch quality control check (QA) in the Can Cleaning Logbook.

7.3. Fill dewar with liquid nitrogen.

7.4. Load canisters in the oven, attaching to the manifold and tighten so canisters do not rotate. Make certain the canister valves are open and the QC sample is easily reached.

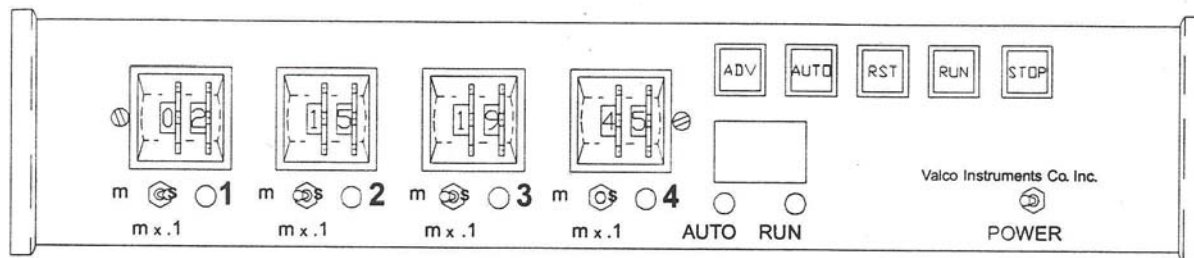
7.5. Set oven heater to no more than 70 degrees centigrade, turn on heater and close the oven doors.

7.6. If cleaning less than eight (8) canisters the unused ports must be capped.

- 7.7. Turn on the vacuum pump, open the nitrogen tank and valves located on top of the humidifying canister. Set the nitrogen tank's second stage regulator between 20 and 25 psig.
- 7.8. Purging Cycle Timer usage
  - 7.8.1 The Valco instrument timers are located on the top of the canister-cleaning oven. Two black boxes make up the complete timing system.
  - 7.8.2 The upper box is used to set the cycle times and to set manual or automatic mode.
  - 7.8.3 Each purge cycle will last for 24 minutes, 12 minutes for evacuating and 12 minutes for pressurizing.
  - 7.8.4 The total cleaning process is a minimum of four purging cycles or a total of 96 minutes.
  - 7.8.5 Set digital switches above light one and light two to 12 minutes (See Figure 1). These represent the evacuating and pressurizing cycle times respectively. The digital switches associated with lights 3 and 4 are set to zero.
  - 7.8.6 The toggle switches located above mx.1 are set to "m" (minutes) for the lights 1 and 2 and set to "s" (seconds) for lights 3 and 4 (See Figure 1).
  - 7.8.7 The lower box is used to set the total cycle time. The number of purging cycles needed determines this. If using four purging cycles then the total time is set to 96 minutes.
  - 7.8.8 The digital switches on the lower box should be set as follows for a purging cycle of 96 minutes: 1, 96, 0, 1, or 1,48,48,0.
  - 7.8.9 Digital switches associated with lights 1 and 4 are used to turn on and turn off the automatic timing sequence while switches associated with lights 2 and 3 are set for total time. Each digital switch is set from 0 to 99 minutes. Therefore the maximum possible time is 198 minutes.
- 7.9 After the upper and lower boxes have been set, press the auto button on the upper timer (See Figure 1). The auto light should come on.
- 7.10 Press the run button on the lower timer (See Figure 1). The first light (1) should light briefly and then switch to light 2. The system will evacuate to – 30 inches Hg for 12 minutes.
- 7.11 Be sure to check the in-line pressure gauge to make certain the system is operating correctly.

- 7.12 At this point the system will switch between vacuum and pressure automatically ending the purging cycle with the canisters being under vacuum (-30 inches Hg).
- 7.13 The canister cleaning system can be manually operated.
  - 7.13.1 Proceed with loading the oven as stated above.
  - 7.13.2 Set the upper box to the desired cycle times.
  - 7.13.3 Using the advance button, activate either the vacuum cycle or pressure cycle.
    - 7.13.3.1 The lights for digital timers 1 and 2 will light indicating which cycle is being used. Also monitoring the pressure gauge will indicate what cycle is being used.
    - 7.13.3.2 Repeat this cycle three (3) times. On the last pressurization cycle, close the valve on the canister to be used as the QC check.
- 7.14 Perform a final canister evacuation, then close the remaining canister valves.
- 7.15 Turn off the vacuum pump, close the humidifier valves, and shut off the compressed nitrogen tank.
- 7.16 Turn off the canister oven heater, allow the canisters to cool to room temperature and then remove the canisters.
- 7.17 Give the QC check canister to the instrument operator for analysis.
- 7.18 Place the remaining unchecked canisters on the shelf located immediately next to the canister-cleaning oven.
- 7.19 After the canisters have been determined to be clean the field sampling sheets are photocopied. One copy is given to the project manager while one copy is placed in the field sampling sheet binder.

FIGURE 1



### Revision History

Version	Date	Changes
1.0	November 15, 2000	Initial Version

## **Appendix 3**

### *Mass Selective Detector Autotune Criteria*



## **Mass Selective Detector Autotune Criteria**

A standard autotune routine is performed on the mass selective detector (MSD) each day prior to sample analysis. The autotune report is evaluated for the following:

1. An unusual change in electron multiplier voltage.
2. Peak width for tune masses should be between 0.4 amu and 0.6 amu.
3. The relative abundance of tune mass 219.0 should be greater than 30% of tune mass 69.0.
4. Isotope abundance ratio for mass 70.0 should be between 0.54% and 1.6%.  
Isotope abundance ratio for tune mass 220.0 should be between 3.2% and 5.4%.
5. Air leaks in the GC/MS system are checked by evaluating the levels of masses 28 and 18 (nitrogen and water).

If autotune criteria are not met the system should be evaluated for problems. After all system problems are resolved, the detector should be autotuned before sample analysis. File the autotune reports in the instrument autotune folder.

## **Appendix 4**

*Calibration Standard Preparation for Carbon Disulfide, MSD-4*

## Calibration Standard Preparation for Carbon Disulfide MSD-4

**The certified stock gas used for calibration during this study was purchased from Scott-Marrin, Inc. and has the following specifications:**

Cylinder No:	FA02705
Expiration date	November 10, 2007
Carbon Disulfide	0.457 PPM/V

Working analysis standard is prepared by diluting the stock gas using the following procedure.

1. A six liter Silco canister is evacuated to –30 inches Hg.
2. 50 ml of carbon disulfide stock is transferred to the canister using a gas tight syringe equipped with a stopcock.
3. 100 µl of reagent grade water is added to the canister using a syringe and syringe adapter.
4. The canister is pressurized to approximately 29.4 psig with grade five or better nitrogen.

The canister will contain CS<sub>2</sub> at the following concentration:

Carbon Disulfide	3.95 µg/m <sup>3</sup>
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The standard sample injection volume is 200 ml. Using the cryogenic sampler to introduce the following volumes of working standard to the GCMS generates a calibration curve.

<u>Volume</u>	<u>Carbon disulfide</u>
200 ml	3.95 µg/m <sup>3</sup>
100 ml	1.98 µg/m <sup>3</sup>
50 ml	0.99 µg/m <sup>3</sup>
25 ml	0.49 µg/m <sup>3</sup>
15 ml	0.30 µg/m <sup>3</sup>